Study of New Fabrication Method for Long-Length Carbon Nanotubes

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ICarbon nanotube (CNT) has excellent properties for use in electric wires and cables. It is expected that CNT achieves lighter weight than aluminum and lower electrical resistivity than copper. The authors propose the "Carbon Transmission Method (CTM)" as the novel production method for realizing higher quality and longer length CNT. In CTM, the supply of carbon source gas and the growth of CNT can be independently controlled in different atmospheres through the use of fibrous catalyst. The authors demonstrated growing CNT on the end of a Fe fibrous catalyst in an isolated Ar gas atmosphere by transmitting carbon along the fibrous catalyst from the other end in a mixed carbon source gas atmosphere (a mixture of CH_4, H_2 and Ar). As the result, the formation of multi-walled CNTs 10 to 50 nm in diameter and over 100 μm in length was observed on the ends of catalyst fibers.

1. Introduction

Recently, the crisis of global warming is being actively discussed around the world. It is known that the main cause of global warming is the increase of greenhouse gases such as CO_2. Suppression of greenhouse gas increase has become an important theme in sustaining social development. Global warming prevention measures being taken include the use of natural energies such as wind and solar power and the implementation of CO_2 capture and geological storage.

At present, copper wires are used in equipment such as power cables, automobiles, home electric appliances and industrial machines. If copper wires are replaced with carbon wires that have the same conductivity as copper wires, weight reduction of aircraft and automobiles will be achieved, which will lead to reduction of energy consumption [(11)].

A carbon nanotube (CNT) has a simple structure composed of a tubular graphite body. It is expected to exhibit an excellent low resistivity equivalent to or lower than that of copper. Furthermore, CNT is lighter in weight than aluminum and higher in strength than steel. These features show that CNT is seen as an innovative material for future electric wires.

Presently, the CNT growth method that is mainly used is the catalytic CVD method [(1)-(5)]. However, CNTs obtained through the catalytic CVD method have been short in length, about 0.1 to 10 mm, and their quality is not so good, with defections in the graphen layers. The CNT growth rate drops with the reaction time and eventually stops in the thermal CVD process [(5)], because unnecessary inhibitory carbon covers the surfaces of nano-sized catalyst particles as a result of the decomposition of carbon source gas as shown in **Fig. 1**. It is difficult to sustain the continuous growth of CNT in a CVD growth process that uses catalyst particles. The growth time in the thermal CVD process is improved by adding a slight amount of water into the source gas so as to remove unnecessary inhibitory carbon from the nano catalyst particles, but this leads to the destruction of the grown CNT [(5)]. This means that the length and the quality of a CNT trade off with each other.

To continuously grow a high quality CNT without defect, carbon source supply and CNT growth on the catalyst should be separated and controlled independently. However, in the CVD process in which nano catalyst particles are used, it is difficult to control the growth of CNT without being influenced by carbon source gas. The author proposes a novel growth process named Carbon Transmission Method (CTM) which can control carbon source supply and CNT growth independently [(6)].

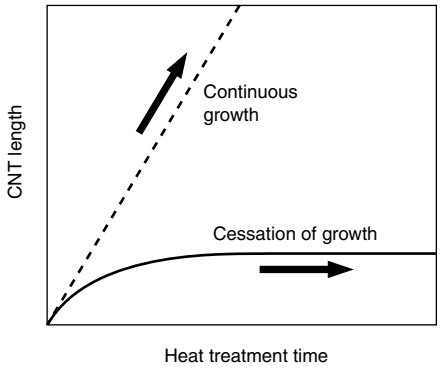

Fig. 1. Heat treatment time dependence of thermal CVD-grown CNT

2. Carbon Transmission Method

Figure 2 shows the concept of CNT growth by the CTM process. In the CTM process, the two functions of catalyst, which are supplying carbon source gas and growing CNT, are separated. The structure of the catalyst for the CTM process is composed of a fibrous catalyst and a non-catalytic separator foil. Therefore, supply of carbon source gas and growth of CNT can be controlled independently by imposing different conditions

at each end of the Fe catalyst fibers penetrating the foil. The concept of the CTM process is as follows:

(1) Carbon source gas can be provided continuously without the formation of inhibiting carbon layers on the ends of the Fe fibers in a controlled atmosphere.

(2) Dissolved carbon diffuses from one end of the Fe fibers to the other end through an Ag foil separator.

(3) CNTs grow continuously on the end of the Fe fibers that reside in an inactive gas such as Ar, and are uninfluenced by the chemical and physical conditions in the carbon source gas.

In the CTM process, the rate of CNT growth may become high along the fine Fe fibers. Usually, diffusion of carbon in bulk Fe is known as carburizing, a process used for hardening of machine parts such as various kinds of gears. In this case, the diffusion rate is slow and about 1 mm/h because of the diffusion in bulk material. Meanwhile, the diffusivity of carbon in the immediate vicinity of Fe grain boundaries has been reported to be about 10^3 to 10^4 times higher than that in bulk Fe [7], [8]. Therefore, carbon for CNT growth can be provided quickly by fast diffusion along the fine fibrous Fe catalyst with a sub-μm thickness. O. Suekane et al. reported on a high growth rate of 220 μm/sec (about 0.8 m/h) at the initial phase of CNT growth [9]. The author expects the continuous growth rate of about 1 m/h in the CTM process.

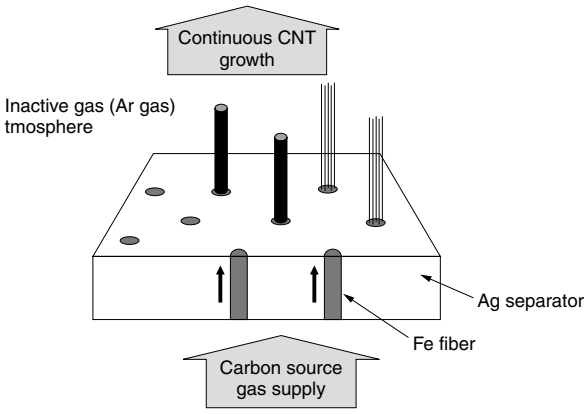

Fig. 2. Conceptual illustration of CNT growth using CTM process

3. Experimental

Figure 3 shows the fabrication process of the catalyst for the CTM process. Fe and Ag were chosen as the inactive materials used in the heat treatment. Pure Fe and Ag metals can be easily formed into fine wires. The CTM catalysts were fabricated by deforming the composite wire composed of an Ag matrix and fine Fe fibers. High-purity Ag pipes (over 99.99 wt%) and high-purity Fe wires (99.998 wt%, RRR_H up to 2000) were prepared, and the composite wire was fabricated by performing the conventional techniques of metal wire drawing and stacking repeatedly in a similar way as the fabrication process of superconducting wires [10]. The fabricated composite wire made of Fe fibers and an Ag matrix 10

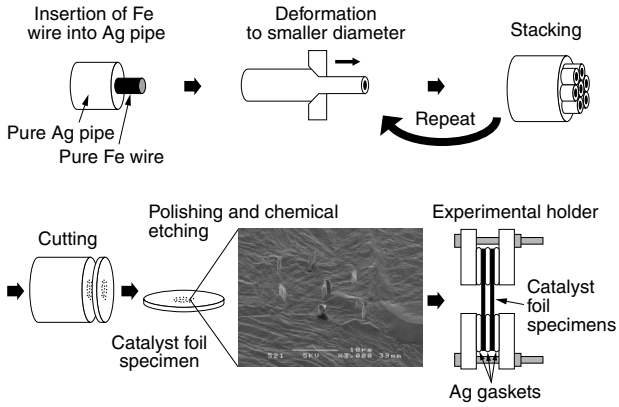

Fig. 3. Fabrication process of catalyst foil specimen for CTM

mm in diameter was sliced into thin rounds and polished until the thickness becomes about 50 μm. The both ends of Fe fibers were exposed over the surface of Ag by chemical etching using a mixed aqueous solution of ammonia and hydrogen peroxide. The Fe fibers were deformed into various tape shapes, as shown in **Fig. 3**. One ends of the catalyst foil specimens were sealed by Ag gaskets, and Ag holders were tightened by stainless bolts. Ar gas was filled into the space in the Ag gasket between the two catalyst foil specimens. The mixed gas (CH_4, H_2 and Ar) was applied as the carbon source gas to the outside of the Ar-gas filled catalyst foil specimens at 850 to 900 deg. C for 1 to 2 hours in 1 atm. The sealing properties for the carbon transmitted side in the holders can be checked after the heat treatment. The sealed space was ballooned by thermal expansion with the increase of temperature from about 300K to between 1,100 and 1,200 K if there is no leak through cracks and clearance at the sealed area of the holder.

After the heat treatments, the C structures formed on the both ends of the Fe filaments were inspected with scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy dispersive X-ray spectrometry (EDS).

4. Result and Discussion

Figure 4 shows the SEM images of the both ends of the Fe fibers on the carbon source gas supply side and the carbon transmitted side of the CTM catalyst foil specimen after the CTM heat treatment process at 850 deg. C for 1 hour. CNTs were not observed on the ends of the Fe fibers in the carbon source gas supply side of the specimen holder after heat treatment in a mixed gas flow (200 cc/min of CH_4, 400 cc/min of H_2, and 400 cc/min of Ar). Instead, graphite grains were observed on the ends of the Fe fibers. In contrast, many CNTs were observed on the ends of the Fe fibers on the carbon transmitted side of the CTM catalyst foil that remained in an Ar atmosphere.

This shows that the growth of CNTs originates from

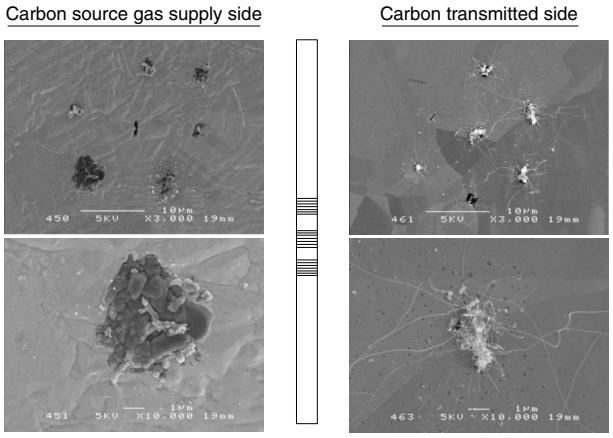

Fig. 4. SEM photographs of Fe fiber ends on CTM catalyst foil specimens after heat treatment of carbon materials

the ends of the Fe fibers. The structures of the CNTs and CNFs were observed with TEM and EDS. The generated CNTs were multi-walled CNTs (MWCNTs), with diameters ranging from about 10 to 50 nm. **Figure 5** shows the TEM images of the CNTs and CNFs grown on the carbon transmitted side. Extra-long fine Fe nano-filaments were found in these CNTs and CNFs. The Fe nano filaments have diameters ranging from several to 10 nm, with length-to-diameter ratios over 20. This indicates that the Fe catalyst was reformed into the Fe nano-filaments on the Fe fibers as the CNTs grew. Such elongation of Fe catalyst nano-filaments is unique to the process of CNT growth by diffusion of carbon into Fe. In the thermal CVD process, it is difficult for the catalyst to form the extra-long nano-filaments of Fe in the CNTs while under the influence of direct carbon source gas supply [12].

Figure 6 shows the TEM photograph of the base area of the lower side CNT shown in **Fig. 5**. The graphen layers were observed up to the center of the CNF filament. The Fe nano-filament was buried in the graphen layers of the CNF filament. **Figure 7** shows the both ends of a CNF that has a Fe nano-filament inside. The diameter of the Fe nano-filament gets smaller at the tip, while that of the CNF changes very little. Moreover, the Fe nano-filament has a larger diameter at the base. A thin, tail-like projection is formed on the base of the Fe nano-filament. The projection is assumed

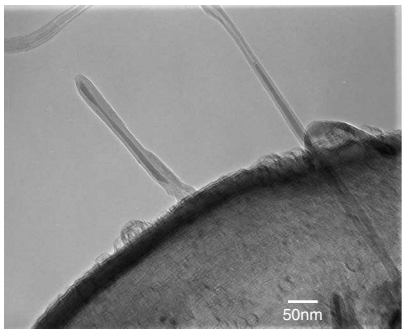

Fig. 5. TEM photograph of CNTs and CNFs by CTM process

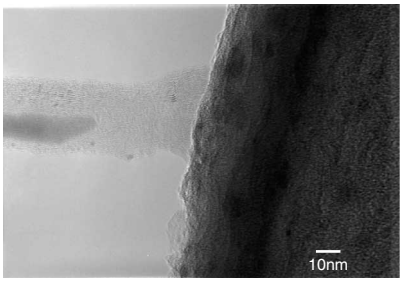

Fig. 6. TEM photograph of base of CNF in Fig. 5

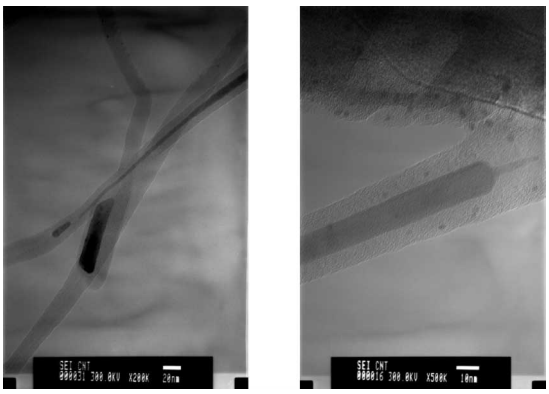

Fig. 7. TEM photographs of CNF with Fe nano-filament taken at (a) tip of Fe nano-filament and (b) base of Fe nano-filament

to be due to the plucking away of the Fe nano-filament during the generation of CNF.

The mechanisms of these phenomena are perceived to be as shown in **Fig. 8**. It is assumed that carbon diffused into Fe fibers at the transmitted side are deposited on the ends of these Fe fibers as CNTs or CNFs that have carbon nano-filaments inside. Hollow structure CNTs were generated when graphen layers were not generated on the tips of the Fe nano-filaments. Non-hollow structure CNFs were generated when graphen layers were generated on the tips of the Fe nano-filaments.

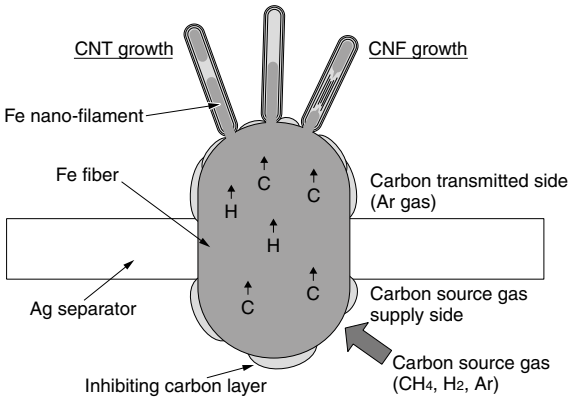

Fig. 8. Observed CNT growth mechanism of CTM process

Figure 9 is the SEM image of the ends of the Fe filaments on the carbon transmitted side of a CTM catalyst foil specimen after CTM heat treatment at 900 deg. C for 2 hours. Many long CNTs with lengths over 100 μm were observed on the CTM catalyst foil surface in the carbon transmitted side. This indicates that the CTM process is highly capable of fabricating longer-length CNTs by controlling various other factors such as the atmosphere in the carbon source gas supply and carbon transmitted sides, the structure of CTM catalyst foil, and the conditions of heat treatment.

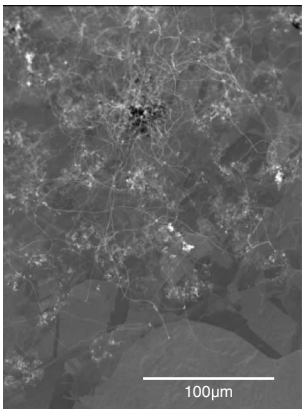

Fig. 9. SEM photograph of CNTs of over 100 μm in length at carbon transmitted side of CTM catalyst foil specimen

5. Conclusions

CNTs with lengths exceeding 100 μm were generated successfully by the Carbon Transmission Method (CTM) process in which the two functions of the catalyst, carbon source gas supply and CNT growth, were separated. After the carbon source gas was provided on the ends of the Fe fibers of the catalyst foil specimens and diffused into the Fe fibers, CNTs were grown on the opposite ends of the Fe fibers. It is indicated that these data will lead to the development of the continuous growth technique of high quality CNTs for various electric wire applications.

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